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Atomistic calculations are performed to study defect energetics in $ZnGeP_2$ where two- and three-body interatomic potentials are used to simulate the perfect lattice. Formation energies for native ionic defects and binding energies for some of the electronic defect-complexes are calculated. The dominance of antisite defect-pairs is predicted in the lattice. However, the defects controlling the spectroscopic properties would seem to be associated with vacancies. For the EPR-active acceptor center, the hole is found to be localized near the zinc vacancy rather than near the zinc antisite. The calculated results suggest that reported Hall effect and photoluminescence data are compatible with the existence of two acceptors where one is significantly shallower, experimentally by 0.27 eV, in reasonable agreement with the calculated difference of 0.37 eV.

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Executive Summary

This documentation is the final technical report for work performed under AFOSR grant F49620-94-1-0228. The title of this project was "Atomistic calculations of defects in $ZnGeP_2$" and the Principal Investigator was Ravi Pandey, Physics Department, Michigan Technological University, Houghton, MI 49931. This was a one-year research program to use atomistic modeling techniques to study defect energetics in $ZnGeP_2$. During the grant's active period, the following reports have been published/submitted for the publication.

(i)   M. H. Rakowsky, W. J. Lauderdale, R. A. Mantz, R. Pandey and P. J. Drevinsky, Symposium A, Proceedings of the Fall meeting of MRS 1994.

(ii)   P. Zapol, R. Pandey, M. Ohmer and J. Gale, 1995, submitted for publication.

Our atomistic approach uses two- and three-body interatomic potentials to simulate the perfect $ZnGeP_2$ in the framework of the shell-model with fractional charges for the constituting ions in the lattice. The lattice and dielectric constants are well described by this potential model. This model is then used to calculate defect energies of several plausible types of ionic and electronic defects using the Mott-Littleton methodology.

Although cation lattice disorder is predicted to be the dominant native defect, the dominant defects controlling the properties of interest would seem to be the zinc acceptor vacancy (binding energy of 0.57 eV) which is partially compensated by a phosphorus donor vacancy (binding energy of 0.68 eV). For the EPR-active acceptor center, the calculated binding energies and lattice distortion corroborates the ENDOR spectrum associating the zinc vacancy with the acceptor center.

I. Introduction

Ternary chalcopyrite semiconductors are known to have large nonlinear optical coefficients making them candidates for second harmonic generation and optical parametric oscillator applications.[1-3] In this group, zinc germanium phosphide ($ZnGeP_2$) is one of the most promising member and has been proposed for 2.05 μm-pumped type-I oscillators.[4-6] However, the presence of an absorption band near the pump wavelength limits the effectiveness of this material for device applications. This absorption band in the spectral region of 1-2μm has been attributed to photo-ionization of a highly compensated deep native acceptor center (referred to as AL1).[7-10] The acceptor is attributed to a zinc vacancy and its binding energy (E_v) is given as 0.4 to 0.6 eV. It is suggested that the compensating donor is a phosphorous vacancy. There is no indication in the literature of its binding energy since it can not be easily determined as all bulk crystals are semi-insulating p-type. In an analogous way, it should be a deep donor since in $CdSiP_2$ the P vacancy donor binding energy (E_c) has been given as 0.63 eV[8] and the P vacancy donor in GaP, the binary analog of $ZnGeP_2$, is estimated as 0.3 eV.[9] The concentration of both acceptors[9] and donors[7] has been typically in the range of 10^{19} cm^{-3}.

The EPR studies on as-grown $ZnGeP_2$ have observed an acceptor center in the lattice with concentrations exceeding 10^{19} cm^{-3}. This EPR-active center (related to the AL1 center) is considered to be associated with the

native defect-complex involving either a zinc vacancy (V_{Zn}) or a zinc ion on a germanium site (Zn_{Ge}).[11] A recent ENDOR study favors the singly ionized zinc-vacancy model.[12] In addition, a photoinduced EPR[13] study indicates that the P vacancy is the dominant donor in this highly compensated material. Thus, the experimental work on defect identification provides support for the traditional model described in the previous paragraph.

Theoretical studies on this material have been limited to perfect lattice only. The results of electronic structure calculations based on density functional theory were compared to x-ray photoemission spectra.[14] A successful attempt has also been made to perform lattice dynamics calculations within the framework of rigid ion model.[15] However, none of the theoretical efforts have been directed to understand the properties of defects in this material. In this paper, we make such an attempt to perform a study on defective $ZnGeP_2$ using atomistic simulation techniques based on the shell model. We will first calculate the energies of Frenkel, Schottky and antisite disorder in the lattice and will simulate the EPR-active acceptor center to provide the microscopic description for its identification. We note here that the shell model calculations have been shown as a highly effective tool for prediction of defect energetics in ionic and semi-ionic materials including sixfold and fourfold-coordinated structures.[16,17]

In the following section, we briefly describe the shell-model and potential parameters to calculate the $ZnGeP_2$ properties. The energetics and structure

of ionic and electronic defects are discussed in Sec. III. The results are summarized in Sec. IV.

II. Perfect Lattice

We begin with the pair-potential description of the perfect lattice consisting of the shell-model ions. The two-body interionic potential energy is then the sum of the long-range Coulombic and the short-range non-Coulombic contributions. We use a simple analytical expression of the Buckingham type for the short-range interaction between ions i and j :

$$V_{ij} = A \, exp \, (-r_{ij}/\rho) - C r_{ij}^{-6}, \qquad (1)$$

where the term in r^{-6} is referred to as the dispersive term.

In the shell-model,[18] each point ion consists of a core of charge X, and a shell of charge Y, such that the total charge is the sum of the core and shell charges. The polarization of a shell-model ion is then described by the displacement of a shell from a core, the two being connected by a harmonic spring with a force constant K.

Potential parameters, both in the analytical representation of short-range interactions (A, ρ and C) and in the shell-model treatment of ionic polarization (Y and K) are obtained by empirical fitting to the crystal structure[19] and known elastic and dielectric constants.[20] The fractional coordinate of the P shell was also taken as a parameter because the location of the

shell in the lattice is unknown.[21] Fitting and all calculations were performed using the program GULP.[22]

$ZnGeP_2$ crystallizes in the chalcopyrite phase with a symmetry space group of D_{2h}^{12}. The chalcopyrite phase can be considered as a superlattice of the cubic zincblende with the $c/a = 2$.[1] It can easily be obtained by replacing each half of cations by Zn and Ge ions respectively, and introducing slight distortion (i.e. $c/a = 1.958$) along z-axis in the zincblende phase (see, Fig.1). The tetrahedral coordination in the $ZnGeP_2$ lattice suggests that the covalent bonding (with sp^3 hybrid bonds) predominates. On the other hand, the composition of the cation sublattice (consisting of Zn and Ge) indicates a significant presence of the ionic character in the bonding.

Realizing this, we therefore do not begin with fully ionic model assuming Zn^{2+}, Ge^{4+} and P^{3-} ions, rather we fit the charges of the constituting ions to experimentally measured crystal constants.[19] In this way, covalency is taken into account by use of the empirical fitting method which yields the fractional charges of +1.2 for Zn, +1.8 for Ge and -1.5 for P. A similar use of fractional charges was proposed in the lattice dynamics calculations of $ZnGeP_2$.[15]

In addition, three-body potentials were used for more accurate treatment of the many-body effects. They were taken in the Axilrod-Teller form,[23] which is derived from third-order perturbation theory as a triple-dipole in-

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teraction:

$$V_{ijk} = k_{ijk} \left(1 + 3 \cos \theta_i \cos \theta_j + \cos \theta_k \right) / R_i^3 R_j^3 R_k^3, \qquad (2)$$

where k_{ijk} is a coefficient, θ_i and R_i are i-th angle and side of the triangle formed by ions i, j and k.

Table 1 lists the potential parameters representing the interionic interactions in the lattice. In this potential model, we neglect the cation-cation short-range interactions and treat the Zn and Ge ions as rigid ions in the lattice. The calculated lattice properties are compared with the experimental data in Table 2. Accordingly, the potential model reproduces the lattice structure very well. The overall good agreement between the calculated and experimental properties for the perfect lattice provides us a sound basis for extending the model to defect calculations. In the absence of experimetal data for elastic constants, we take guidance from the lattice dynamics calculations where a phenomenological rigid ion model with partial ionic charges was used to reproduce the vibrational spectrum of $ZnGeP_2$.[24]

III. Defects

Defect energies of several plausible types of ionic and electronic defects have been calculated using the Mott-Littleton methodology.[25] Here, the lattice containing a defect is divided into two regions. Atoms in the inner region (immediately surrounding the defect) are treated explicitly and allowed to

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relax during the minimisation procedure. The response of the outer region is obtained using macroscopic dielectric theory. In the present calculations the inner region consists of approximately 150 atoms. An increase of this region size introduces the change in defect energies less than 0.03 eV showing a satisfactory accuracy of our results. Note that given adequate pair-potential description of the lattice, these calculations have been proven to provide reliable values of defect energetics.[17]

The calculated Schottky, Frenkel and antisite pair formation energies are listed in Table 3. In $ZnGeP_2$, the Schottky defect is $(V_{Zn}+V_{Ge}+2V_P)$, the Frenkel defect pairs are $(V_{Zn}+Zn_i)$, $(V_{Ge}+Ge_i)$ and (V_P+P_i) and the antisite pair in the cation sublattice is $(Zn_{Ge}+Ge_{Zn})$. As shown, the lowest formation energy comes out to be for $(Zn_{Ge}+Ge_{Zn})$ antisite pair. The magnitude of this energy is small (0.25 eV) suggesting that appreciable disorder would occur in the cation sublattice at higher temperatures. These antisite defects are then followed by the Frenkel pairs of Zn and Ge. For Schottky pair, the large formation energies would seem to preclude their existence as intrinsic point defects in the lattice.

Experimentally, electronic defects including both electron and hole centers in as-grown $ZnGeP_2$ have been identified by the magnetic resonance studies. An EPR spectrum associated with a hole center was first observed by Kiel[26] who suggested the center to be P_2^{5-}, analogous to the V_k center in halides. Recently, Rakowsky et al. have performed a detailed study

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of the angular dependence of the EPR spectrum suggesting that either a zinc vacancy or a zinc ion on a germanium site forms the acceptor center. Their hyperfine analysis indicates that the hole is equally shared between two near-neighbor phosphorous ions.[11] A recent ENDOR study favors the singly ionized zinc-vacancy model based on the requirement of a large lattice distortion near the defect complex.[12] It was suggested that the observed change in the angle between inter-phosphorus axis and the basal plane of the crystal can only be due to the presence of the zinc vacancy.

For calculations, we follow a similar approach proposed first for tetrahedrally coordinated semiconductor, ZnSe.[16] Our aim is to obtain binding energy and lattice distortion in both the possibilities for the acceptor center i.e. a hole may be trapped near a zinc vacancy forming a center similar to the V^- center in oxides[27] or may be localized in the vicinity of an antisite defect, Zn_{Ge}. Since the EPR specta clearly identifies the hole be shared equally by a pair of near-neighbor phosphorous ions, its binding energy is then

$$BE = TE(h2 + D) - TE(h2) - TE(D), \qquad (3)$$

where D is either V_{Zn} or Zn_{Ge} and TE refers to the total energy of the defect-complex. Furthermore, we also consider the cases where either the hole is localized near only one of the near-neighbor P ion (i.e. 1-center case) or distributed over all of the near-neighbor P ions (i.e. 4-center case). In these calculations, we assume that the trapping of a hole only changes

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long-range Coulombic interactions. Short-range interactions between P ions sharing the hole and the surrounding ions are taken to be that of the perfect lattice.

Table 4 lists the calculated binding energies of the hole centers in $ZnGeP_2$. The binding energy of a hole shared by two near-neighbor P ions (i.e. 2-center case) comes out to be much larger in the vicinity of the Zn vacancy than that of the Zn_{Ge} site. This clearly demonstrates that the $(h2+V_{Zn})$ defect complex is relatively more stable in the lattice. Comparing the binding energies for different hole localization regions in both Zn vacancy and antisite cases we can see a striking distinction. The hole tends to be localized near Zn vacancy, i.e. the more hole is localized, the larger is binding energy. But the trend is exactly opposite for the antisite defect and a hole cannot be localized near the Zn_{Ge} site. Thus, the acceptor center can only be stabilized by the Zn vacancy in the lattice. This conclusion is also supported by the defect geometry considerations in the lattice. For $(h2+V_{Zn})$, the nearest neighbor P ions relax significantly (12% of a bond length) towards the vacancy, whereas only a small relaxation (2% of a bond length) occurs for these ions for the $(h2+Zn_{Ge})$ defect complex. The results therefore show that the the association of the zinc vacancy introduces a very large distortion in the lattice corroborating the analysis of the ENDOR spectrum. We also note here that the acceptor binding energy comes out ot be 0.57 eV as compared to the experimental value of 0.5-0.55 eV obtained from temper-

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ature dependence of the Hall effect or of the resistivity.[7,28] On the other hand, analysis of IR absorption spectra generally gives a value in the range of 0.6-0.7 eV.[29]

For the acceptor center associated with the Ge vacancy, the calculations predict binding for the hole only in the 1-center model. For the 2- and 4-center cases, the defect-complex is not stable (Table 4). There is no experimental observation that the V_{Ge} defect-complex whose stability we calculate exists. The litreture just does not address the possibility that two native acceptors exist. However, it is possible to re-interpret past data in light of this result. If the V_{Ge} defect is well compensated, then Hall effect data would reveal only the deeper V_{Zn} defect. On the other hand, if the V_{Ge} defect is only partially compensated, the Hall data would reveal its activation energy, or in the special case that the defect is nearly exactly compensated, the apparent activation energy from a two level acceptor-donor analysis would be the average of the deeper and shallower energy. Using the energies in Table 4 as an example, one could expect to see a range of Hall activation energies (i.e. 0.2, 0.35 and 0.57 eV) due to changes in the compensation level.

Sodeika et al.[8] have reviewed observed Hall activation energies ranging from 0.3 to 0.57 eV in $ZnGeP_2$. Using a two level model, they have attributed this variation to interactions with a nearby compensated donor at high compensation levels which has the effect of moving the isolated activation energy from the deeper value to the shallower value. In a three level

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model such a change in Hall activation energy can be explained by varying the compensation ratio of the shallower acceptor from less than one to greater than one. Very clear examples of shallow Hall activation energies ranging from 0.31, 0.33 and 0.35 eV are referenced.[8] This could be interpreted using a three level model as a case where the partially compensated shallow V_{Ge} defect activation energy of 0.31-0.35 eV is being observed directly. When it is overcompensated the activation energy of 0.50-0.57 eV of the V_{Zn} defect is observed. Past photoluminescence studies of $ZnGeP_2$ may also have revealed the V_{Ge} defect as compensated centers. For example, in a massive study of over a 100 samples grown in different ways and variously doped Averkieva et al.[30] report that luminescence is generally seen at approximately 1.6 and 1.3 eV attributed to two levels located 0.49 and 0.79 eV from a band edge. In a three level model, we suggest that the 1.6 eV recombination energy could be attributed to the V_{Ge} defect and 1.3 eV to the V_{Zn} defect. Therefore, reported Hall effect and photoluminescence data are compatible with a three level model (i.e. two acceptors and one donor) where one of the acceptor is significantly shallower, experimentally by 0.27 eV, in reasonalble agreement with the calculated difference of 0.37 eV.

While the zinc vacancy is the dominant acceptor in $ZnGeP_2$, the phosphorous vacancy(V_P^0) is found to be the dominant donor in the as-grown material that is associated with a photo-induced EPR center in the lattice.[13] The proposed model for this EPR-center suggests that two zinc ions

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neighbouring to the phosphorous vacancy unequally share an unpaired spin. At present, electron density distribution calculations are beyond the limitations of this atomistic shell model. However, we can calculate the binding energy of the defect complex assuming an equal sharing of the electron by two zinc atoms near the P vacancy. The binding energy comes out to be about 0.68 eV showing that the EPR-center is very stable in the lattice.

Finally, in many previous studies[14,15] the chalcopyrite phase was replaced by the zincblende phase, assuming that the small distortion along z-axis does not significantly contribute to the $ZnGeP_2$ properties. We verified this point using identical potential parameters for the zinc blende phase. Defect energies for both phases show a very similar trend. We may therefore conclude that the consideration of zincblende as the structural analog of chalcopyrite is also valid for defects calculations.

IV. Summary

The work described here has demonstrated that $ZnGeP_2$ can be simulated successfully in the framework of the shell-model with fractional charges for the constituting ions in the lattice. The lattice and dielectric constants are well described by this potential model.

The calculated defect energies and lattice distortion corroborates the ENDOR spectrum associating the zinc vacancy with the acceptor center in $ZnGeP_2$ and the calculated binding energies for it are in agreement with

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values reported from absorption and Hall effect measurements. The binding energy of the P vacancy donor has been found to be deep as anticipated and its value of 0.68 eV is reported here for the first time.

On the other hand, cation sublattice disorder in the form of antisite defect pairs is predicted to be the dominant native defect on the basis of formation energies. If antisites are present in large concentration their behavior must be quite benign. From our calculations, a hole cannot bind to a Zn antisite so this defect cannot behave as an acceptor as generally expected.[11] If there is a similar inability to bind a charge carrier to the Ge antisite, then antisites will not play a dominant role in determining the properties of the material.

There is no direct evidence that the Ge vacancy acceptor defect whose properties we calculated exists. However, reported Hall effect and photoluminescence data are shown to be compatible with the existence of two accptors where one is significantly shallower, experimentally by 0.27 eV, in reasonable agreement with calculated difference of 0.37 eV. Furthermore, we note here that the observed cation vacancy defect corresponds to the cation with the larger ionic radius in diamond-like semiconductors as a result of a size mismatch driven process to minimize strain. Examples are HgCdTe, $CuInSe_2$, $CuInS_2$, $CdGeAs_2$, and $CdSiP_2$.

The dominant defects controlling the properties of the material would seem to be the Zn vacancy with a binding energy of 0.57 eV which is partially

compensated by a P donor vacancy which has a binding energy of 0.68 eV. However, a three level model which includes the shallower Ge vacancy acceptor defect which is usually overcompensated cannot be ruled out.

IV. Acknowledgements

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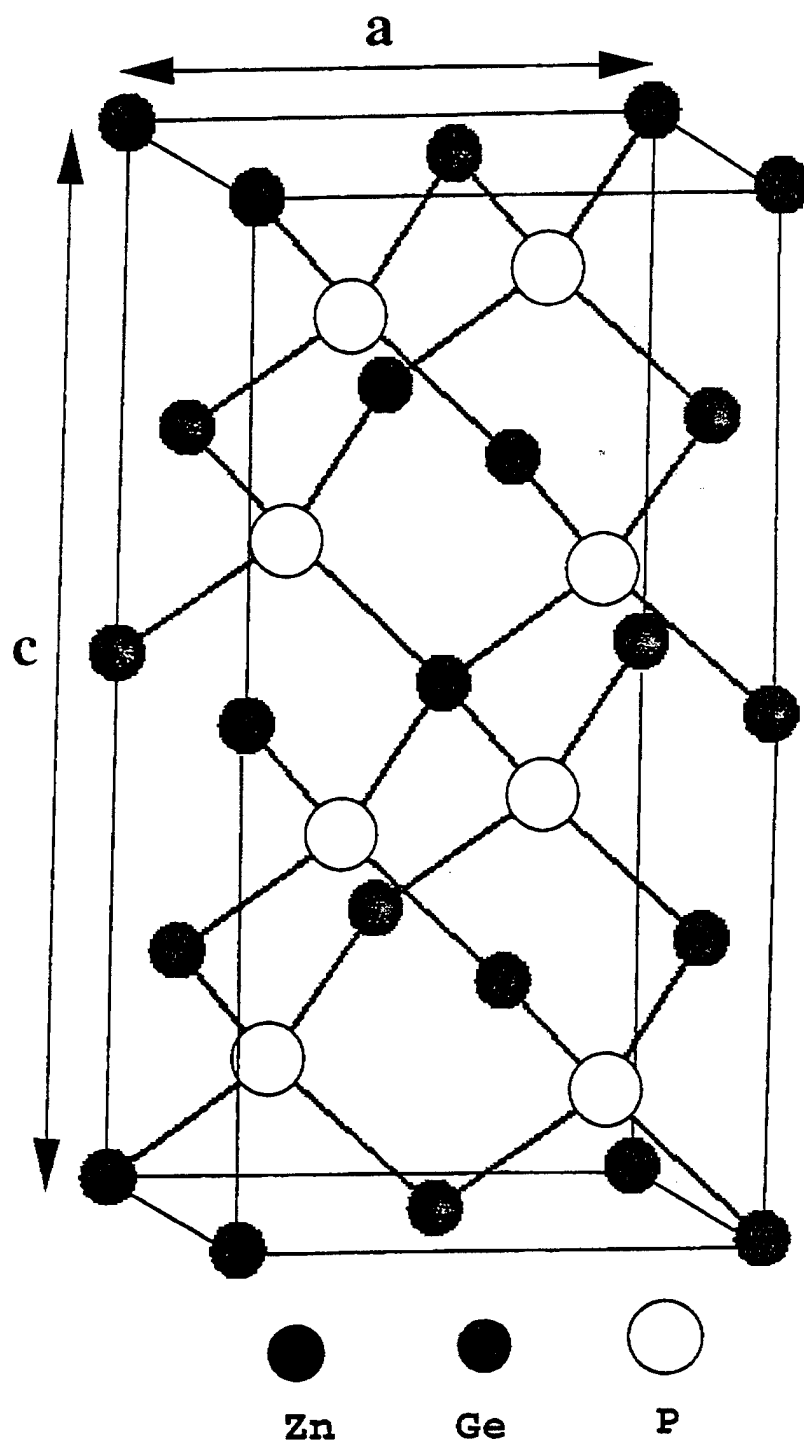
Fig. 1 :   Crystal structure of ZnGeP$_2$.

Zn   Ge   P

Table 1: Two-body and three-body short-range interaction and shell-model parameters for $ZnGeP_2$. The charges on ions are taken to be -1.5e, 1.2e and 1.8e for P, Zn and Ge respectively.

	$A(eV)$	$\rho(\text{Å})$	$k(eV\text{Å}^{-9})$	$Y(e)$	$K(eV\text{Å}^{-2})$
Ge_c-P_s	328.03	0.3937			
Zn_c-P_s	675.61	0.3243			
P_s-P_s	52905.81	0.2795			
P_s-P_s-P_s			1241.15		
Ge_c-P_s-P_s			-99.37		
Zn_c-P_s-P_s			-258.9		
P_c-P_s				-1.674	1.01

Table 2: Calculated and experimental bulk properties of ZnGeP$_2$.

Property	Calculated	Experimental
Lattice constants, Å		
a	5.462	5.467[a]
c	10.717	10.715[a]
c/a	1.962	1.958
Elastic constants, dyn cm^{-2}		
C_{11}	8.32	8.7[b]
C_{12}	4.47	6.6[b]
C_{13}	4.91	6.4[b]
C_{33}	8.34	8.1[b]
C_{44}	3.50	2.9[b]
C_{66}	3.23	2.8[b]
Dielectric constants		
ϵ_0 11	10.89	11.21[c]
ϵ_0 33	12.15	11.40[c]
ϵ_∞ 11	9.44	9.75[c]
ϵ_∞ 33	9.89	9.91[c]

a. Ref. [19].

b. Values from lattice dynamics calculations, Ref [24].

c. Ref. [20].

Table 3: Defect formation energies in $ZnGeP_2$.

Defect	Formation energy, eV
Antisite pair $(Zn_{Ge}+Ge_{Zn})$	0.25
Frenkel pair	
Zn	2.2
Ge	4.1
P	9.3
Schottky pair	17.4

Table 4: Binding energies of electronic defects in $ZnGeP_2$. (The positive values indicate the stability of the defect complexes in the lattice.)

Defect	Binding energy, eV
Hole near V_{Zn}	
1-center	0.57
2-center	0.35
4-center	0.12
Hole near Zn_{Ge}	
1-center	-0.01
2-center	-0.08
4-center	0.17
Hole near V_{Ge}	
1-center	0.20
2-center	-0.18
4-center	-0.35
Electron near V_P	
2-center	0.68